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Methylboric Acid and its Anhydride; The Methylboron Fluorides

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Although numerous mono aryl and alkyl boric acids have been prepared and studied, the simplest compound in this class, methylboric acid, has been missing. Since the first member of a series often exhibits properties which are more readily intelligible (from a fundamental viewpoint) than those of more complex members, it seems important to study such prototype compounds. In particular, methylboric acid has been assumed to be a product in the hydrolytic analysis of certain methylboron compounds[2]; although this assumption seemed to represent an unavoidable conclusion, it still seemed valuable to isolate and study the material involved.

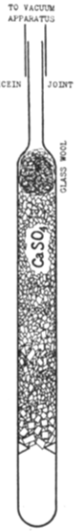

Fig. 1.

The present investigation of the chemistry of methylboric acid and its anhydride brings forth some new knowledge concerning the dative bond (a type of linkage which is illustrated with unusual simplicity by certain compounds of boron), and also adds to the list of solvolytic ring-splitting reactions. Another consequence of the study is a very efficient method of preparing the methylboron fluorides.

Preparation of Methylboric Acid and its Anhydride.—A sufficient quantity of methylboric acid was prepared by the method employed by Khotinsky and Melamed[3] in their nearly successful attempt: namely, the action of methylmagnesium iodide upon methyl borate. The details of the procedure were essentially those described by Snyder, Kuck and Johnson,[4] for other alkylboric acids. The major part of the ether was distilled off through a fractionating column, and the volatile residue then was introduced into the high vacuum apparatus[5] by sublimation at room temperature. This product next was separated from water and ether by a process of fractional condensation. Its vapor tension at 25° was approximately 3 mm.

The material thus isolated did not seem to be a pure substance, and the question whether the fault was due to instability or to a trace of water, could not be answered immediately. The problem finally was solved through the complete dehydration of the crude product, and the study of the effect of water upon the resulting anhydride.

The Dehydration of Methylboric Acid.—A drying agent suitable for removing water from methylboric acid was not found immediately. Bases obviously could not be used. Acid anhydrides also were soon rejected, because they absorbed the product, possibly through formation of mixed anhydrides. The agent finally chosen was gently dried calcium sulfate.[6] Small lumps of the di-hydrate (ordinary plaster of Paris) were placed in a tube having the shape pictured in Fig. 1. This tube then was heated to 200° and pumped for half an hour by a water-jet aspirator; finally it was attached to the vacuum apparatus and pumped further at 200°. After the drying agent had cooled to room temperature, the lower end of the tube was immersed in liquid nitrogen, and the methylboric acid was allowed to sublime toward that point. After its arrival in the form of anhydride, in the bottom of the tube, the rather volatile product was passed back over the calcium sulfate, and condensed in another part of the vacuum apparatus. Separation from residual methylboric acid was managed easily by direct distillation.

Even such an inert drying agent as calcium sulfate absorbed important quantities of the product, and the material thus held back could be recovered only as a mixture of methylboric acid and water, by re-heating the tube *in vacuo*. It was thus found best to use as little as one-fourth of the calculated quantity of calcium sulfate, and to repeat the operations of renewing the drying agent, separating the acid from water, and forming the anhydride, as often as required.

Physical Properties of the Anhydride.—Methylboric anhydride melts at −38° (*in vacuo*). Extrapolation from its vapor tensions gives the value 79° for its normal boiling point. These vapor tensions, measured by the aid of a device described earlier for such purposes,[7] and corrected for the varying density of mercury, appear in Table I. The calculated values came from the equation $\log_{10} p_{(\text{mm.})} = 8.307 - (1909/T)$,

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[1] The data presented in this paper were obtained chiefly during the author's period of work at the University of Chicago. The writing, much of the analysis of the experimental records, and a certain amount of rechecking, were done at the author's present address, the University of Southern California.

[2] Schlesinger and Walker, THIS JOURNAL, **57**, 621 (1935); Schlesinger, Ritter and Burg, *ibid.*, **60**, 1296 (1938); Schlesinger, Flodin and Burg, *ibid.*, **61**, 1078 (1939).

[3] Khotinsky and Melamed, *Ber.*, **42**, 3095 (1909).

[4] Snyder, Kuck and Johnson, THIS JOURNAL, **60**, 107 (1938).

[5] Apparatus of the type described by Stock in *Ber.*, **54A**, 142 (1921), and in "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; *cf.* also footnote 2.

[6] Hammond and Withrow, *J. Ind. Eng. Chem.*, **25**, 653 (1933).

[7] Burg and Schlesinger, THIS JOURNAL, **59**, 785 (1937).

TABLE I

VAPOR TENSIONS OF METHYLBORIC ANHYDRIDE

Temp. (°C.)	0.0	14.3	18.9	21.7	24.8	32.2	39.9	47.7	54.8
$p_{(\text{mm.})}$ (obsd.)	20.5	46.5	58.0	67.8	79.2	113.0	161.5	227.1	304.7
$p_{(\text{mm.})}$ (calcd.)	20.7	46.2	58.7	67.8	79.1	113.2	161.3	227.0	305.3

which implies that the molar heat of vaporization would be 8725 cal., and the Trouton constant, 24.8. The high value of the latter may be due to the van der Waals effects mentioned below.

The Molecular Weight of the Anhydride.—Methylboric anhydride has a molecular weight corresponding to the trimeric formula $(CH_3BO)_3$. This result was to be expected, in view of the known trimeric character of phenylboric anhydride,[8] and of certain higher alkylboric anhydrides.[4]

A 0.0565-g. sample of methylboric anhydride was measured as 10.00 cc. of gas at standard conditions[9] (corrected pressure, 87.5 mm. at 98°; apparatus volume, 118.0 cc.). The molecular weight thus was 126.8 (calcd. value, 125.55, for the trimer).

The compound evidently deviates quite appreciably from the perfect gas law, for samples whose volumes were measured at room temperature (at pressures below 70 mm.) gave the high molecular weight values 129.2 and 129.1. All volumes of samples taken for analysis, or for other quantitative studies, were corrected in accordance with the known tendency for deviation.

The Analysis of Methylboric Anhydride.—The compound was broken down for analysis, by two methods: oxidation to boric acid by chlorine in the presence of water, and complete oxidation by concentrated nitric acid. In each case, the reaction took place in a sealed Pyrex bulb.

(1) A 17.2-cc. sample of the anhydride, with 200 cc. of chlorine and 1 cc. (liquid) of water, was heated for two hours at 100°. Then the excess chlorine, along with any other material more volatile than water, was removed by distillation *in vacuo*. Strong acids now were neutralized (sharp methyl red end-point); finally the boric acid was titrated, in the presence of mannitol, to the phenolphthalein end-point. The quantity of boron was equivalent to 51.4 cc. of gas (theory, 51.6).

(2) A 10.3-cc. sample of the anhydride, with 0.55 cc. of liquid nitric acid, was heated for three hours at 300°, to yield 31.0 cc. of carbon dioxide (theory, 30.9) and 32.0 "cc." of boric acid (theory, 30.9).

These results, taken with the molecular weight, evidently verify the formula $(CH_3BO)_3$.

The Preparation of Pure Methylboric Acid.—It was now found possible to prepare samples having the exact composition of methylboric acid, $CH_3B(OH)_2$, by treating the anhydride with a deficient quantity of water, and then removing the excess anhydride by distillation. The results are expressed by the equation $(CH_3BO)_3 + 3HOH \rightarrow 3CH_3B(OH)_2$. The evidence is against the occurrence of any partial hydration of the trimeric anhydride.

Thus 12.40 cc. of water vapor and 7.47 cc. of the anhydride (both measured in the wholly immersed bulb[7] at 99°) were left together for an hour in a closed tube. After cooling to −80°, and then warming to −26°, the excess anhydride was distilled away at the latter temperature, and measured as 3.32 cc. Hence the 12.40 cc. of water had reacted with 4.15 cc. of the anhydride (theory, 4.13).

The Volatility of Methylboric Acid.—Further evidence that methylboric acid is a chemical individual came from a study of its vapor–solid equilibrium pressures. The results, presented in Table II, determine the equation $\log_{10} p_{(\text{mm.})} = 11.813 - (3404/T)$, from which the calculated values were derived. As shown below, the vapor of methylboric acid is extensively dissociated; this fact, along with the variable character of the melting range, makes it very difficult to estimate the boiling point. It might be near 100°.

TABLE II

VAPOR–SOLID EQUILIBRIUM OF METHYLBORIC ACID

Temp., °C.	25	31	41	45	57	61	65
$p_{(\text{mm.})}$ (obsd.)	2.5	4.2	9.3	13.0	31	42	55
$p_{(\text{mm.})}$ (calcd.)	2.46	4.13	9.38	12.9	31.5	41.8	55.2

Two attempts to obtain the melting point of methylboric acid served only to suggest that the idea of a true melting point here is meaningless. A freshly prepared sample contained in a sealed tube (without air) melted in the range 95–100°. After cooling, the new crystals, which appeared as long, thick blades, had a melting range of 73–77°. The liquid form may have been an uncertain mixture of methylboric acid with its decomposition products.

The Vapor-Phase Decomposition of Methylboric Acid.—A study of the vapor-phase equilibrium system derived from the anhydride and

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[8] Kinney and Pontz, THIS JOURNAL, **58**, 197 (1936).

[9] In this paper, the volume given for a vapor or gas always is referred to standard conditions.

TABLE III

DISSOCIATION OF THE VAPOR OF METHYLBORIC ACID

Anhydride, cc.	Water vapor, cc.	Apparatus vol., cc.	Total pressure, mm., corr.	Temp., °C.	$K_{atm.}$ (exptl.)	$K_{atm.}$ (calcd.)
4.15	12.40	119.4	131.9	99.6	0.268	0.269
4.15	20.72	119.8	197.2	99.7	.282	.270
4.23	11.65	119.6	126.5	99.6	.270	.269
19.80	11.65	119.6	256.5	99.6	.256	.269
6.05	5.14	118.1	90.0	90.6	.201	.197
4.23	11.65	119.4	120.4	84.4	.156	.158
6.05	5.14	119.5	84.75	75.9	.111	.114
6.05	5.14	119.5	83.67	71.7	.103	.098

water showed that methylboric acid exists not only in the solid condition, but also in the vapor state. The assumption that the only reaction here involved is $3CH_3B(OH)_2 \rightleftarrows (CH_3BO)_3 + 3HOH$ led to mutually consistent values of the dissociation constant for widely different compositions, and it was even possible to derive a fairly satisfactory expression for the standard free energy of the dissociation. Attempts to fit other assumptions to the experimental results led only to absurdities.

The equilibrium was studied by making measurements of the total pressure exerted by the mixed vapors. For this work, the device for determining vapor pressures at elevated temperatures[7] again was used. For some experiments, stoichiometrically pure methylboric acid was employed; for others, separately measured samples of water vapor and the anhydride simply were heated together in the immersed bulb. In most cases, the total pressures were measured at several different temperatures, all above the condensation point. The observed values were corrected to the density of mercury at 0°, and, whenever it was proper, for the partial pressure of mercury vapor.

From the total pressure, the known capacity of the apparatus, and the original volumes[9] of the anhydride and water, the partial pressure (in atmospheres) of each of the three assumed components, water, methylboric acid, and the anhydride, was calculated. The dissociation constant then was computed according to the definition $K_{atm.} = P_{anhyd.} \times P_{water}^3/P_{acid}^3$. The conditions and results of the experiments are summarized in Table III.

The values of K obtained from these experiments determine the equation $\log_{10} K_{atm.} = 4.877 - (2030/T)$, from which the calculated values in Table III were obtained. This implies that $\Delta H = 9300$ cal., and $\Delta F° = 9300 - 22.31T$.

The chief source of inconsistency in the experiments at the higher temperatures probably was the uncertainty in the correction for mercury vapor, with which the space in the bulb may not always have been fully saturated. The maximum error might have been 0.2 mm., and this would fully account for the mutual deviations in K at 99.6–99.7°. The greater consistency of the values at lower temperatures probably is due to the smaller uncertainty in the corrections applied to the cathetometer readings (in themselves precise to 0.02 mm. or better).

It does not seem feasible to estimate the extent to which van der Waals attractions may have contributed to the energy values here derived. It is probable, however, that these effects were largely cancelled out, since the volume of each sample was determined by measuring the pressure which it exerted at 99°, in the same bulb which later was used for the equilibrium measurements. In any case, the main conclusion, that water, methylboric acid, and the anhydride are the only substances appreciably involved in the equilibrium, seems quite secure.

The Addition of Ammonia and Trimethylamine to Methylboric Anhydride.—In contrast to the strictly hydrolytic action of water, ammonia and trimethylamine form addition compounds with methylboric anhydride, without destruction of its trimeric character. The compounds $(CH_3BO)_3 \cdot NH_3$ and $(CH_3BO)_3 \cdot N(CH_3)_3$ are fairly stable; far less so is the diammoniate, $(CH_3BO)_3 \cdot 2NH_3$. Neither a tri-ammoniate nor a di-aminate could be shown to exist.

The Ammoniates.—The experimental work establishing the existence of the two ammoniates is summarized in Table IV. The sample of anhydride here employed had a volume of 9.25 cc.[9] The existence of the monoammoniate was obvious, since the removal of excess anhydride (first line) left a material of that composition, having a minimal pressure. The diammoniate is to be recognized from the data of the third, fourth, and fifth lines. The ab-

TABLE IV

PRESSURES IN THE SYSTEM $(CH_3BO)_3$–NH_3

Temp., °C.	Total NH_3 employed, cc.	Pressure, mm.	NH_3 in cond. phase, cc.	Ratio of NH_3 to $(CH_3BO)_3$
0	4.86	19	4.86	0.525
0	9.36	1	9.29	1.004
0	18.5	15	17.5	1.90
0	18.2	12.3	17.4	1.88
0	11.8	11.5	11.0	1.19
0	42.2	348	19.2	2.08
0	75.9	851	19.5	2.10
−45.7[a]	75.9	391[b]	48.0	5.19
−45.7	48.1	325	25.2	2.72
−45.7	42.7	313	20.7	2.24

[a] Maintained constant by a bath of melting chlorobenzene. [b] This is very close to the vapor tension of pure ammonia.

TABLE V

SEARCH FOR SECONDARY AMINATES OF $(CH_3BO)_3$

Temp., °C.	$(CH_3BO)_3$, cc.	Total amine employed, cc.	Pressure, mm., corr.	V. t. of pure amine, mm.	Amine in condensed phase, cc.	Ratio of amine to $(CH_3BO)_3$
0	5.1	38.9	501	680	5.1	1.00
−10	5.1	38.9	399	476	11.9	2.34
−10	5.1	35.4	398	476	8.4	1.65
−45.7	12.1	25.3	72.7	76.5	17.2	1.42
−45.7	12.1	69.3	72.7	76.5	49.1	4.05

sorption of ammonia at the composition 1.90 (third line) and its removal at 1.19 (fifth line), were very slow processes, and the pressures finally established probably do not represent perfect equilibria. More trustworthy is the decomposition pressure 12.3 mm. (fourth line), which was established (from the low side) during ninety-five minutes, and thereafter was observed as constant during two days.

The remaining data in Table IV indicate that no triammoniate is to be recognized by the study of pressure-composition isotherms. There is, however, some indication of a solid solution.

The equilibrium pressures over the two ammoniates were observed at various temperatures: the diammoniate registered 12.3 mm. at 0°, 36 mm. at 17°, and 101 mm. at 26°; the values for the mono-ammoniate were 1.4 mm. at 33°, 3.2 mm. at 50°, 4.3 mm. at 55°, 13.7 mm. at 73°, and 57 mm. at 82°. The failure of the logarithmic law here may well be due to an ammonolytic break-down of the trimer at higher temperatures; just as water splits the anhydride to form $CH_3B(OH)_2$, so might ammonia split it with more difficulty, to form CH_3BOHNH_2. A proof of this hypothesis would require measurements of precision somewhat higher than the present technique affords.

The Trimethylaminate of Methylboric Anhydride.—In the first of a series of experiments, 17.8 cc. of trimethylamine and 5.1 cc. of the trimeric anhydride were condensed together and warmed slowly to room temperature. The excess trimethylamine now was recovered by distillation *in vacuo* at −80°, and measured as 12.7 cc. The residue consisting of 5.1 cc. each of anhydride and amine was an easily sublimable white solid which melted sharply at 67°. The formula $(CH_3BO)_3{\cdot}N(CH_3)_3$ thus seemed justified.

The ease of removal of the excess trimethylamine at −80° made it evident that a secondary aminate would not be easily recognizable. An actual search for such a compound, by the study of pressure-composition isotherms, led only to the solubility effects indicated by the data in Table V. According to the lowering of the vapor tension of the amine, the mono-aminate is five mole per cent. soluble at −45.7°, and sixteen mole per cent. soluble at −10°.

The Volatility of the Mono-aminate.—The equilibrium pressures of vapors over the mono-aminate, observed at various temperatures above and below the melting point, are given in Table VI. These results determine the equation $\log p = 10.520 - (3088/T)$ for the *liquid* and the equation $\log p = 13.158 - (3984/T)$ for the *solid*. These equations indicate 18,210 cal. for the heat of sublimation and 14,114 cal. for the heat of vaporization of the liquid. The heat of fusion thus is estimated to be 4100 cal./mole. These heat values were not corrected for vapor-phase dissociation (described in the next section), because of the uncertainty in the degree of dissociation at the condensation points. The triple point is calculated to be 66.6°, in fair agreement with the observed value, 67.4°. The "boiling point" is predicted to be 131°.

TABLE VI

EQUILIBRIUM PRESSURES OVER $(CH_3BO)_3{\cdot}N(CH_3)_3$

Liquid			Solid		
t, °C.	*p*(mm.) (obsd.)	*p*(mm.) (calcd.)	*t*, °C.	*p*(mm.) (obsd.)	*p*(mm.) (calcd.)
65.0[a]	24.0	24.4	25.9	0.69	0.68
68.1	29.5	29.5	30.2	1.04	1.05
74.2	41.4	42.5	31.0	1.14	1.14
79.1	56.9	56.5	40.0	2.68	2.70
81.4	63.9	64.4	44.9	4.26	4.27
85.5	80.1	81.1	45.7	4.56	4.58
92.3	117.5	117.2	54.9	10.35	10.38
100.5	177.8	179.5	58.2	13.66	13.58
			(65.0)	(24.0)	(23.7)

[a] Supercooled liquid.

Dissociation of the Vapor of the Mono-aminate.—A 12.12-cc. sample of the compound $(CH_3BO)_3{\cdot}N(CH_3)_3$ was confined in a completely immersed bulb[7] and the pressure was measured at each of a number of different temperatures above the condensation point. The degree of dissociation and the dissociation constant, defined according to the equation $(CH_3BO)_3{\cdot}N(CH_3)_3 \rightleftarrows (CH_3BO)_3 + N(CH_3)_3$, were calculated from each pressure value, as shown in Table VII. The values of $K_{\text{atm.}}$ do not clearly follow the van't Hoff equation, and it is reasonable to doubt that the attraction of amine for anhydride, in the vapor phase, is purely chemical. Nevertheless, the observed deviations from 100% dissociation seem too large to be attributed solely to van der Waals effects, and it seems probable that the aminate exists as a vapor.

TABLE VII

VAPOR-PHASE DISSOCIATION OF THE MONO-AMINATE (12.12 cc.)

Temp., °C.	Bulb, cc.	Pressure, mm., corr.	Pressure calcd. for 100% dissociation	Dissociation, %	$K_{\text{atm.}}$
103.3	120.1	191.9	211.6	81.4	0.49
105.5	120.2	196.7	212.4	85.2	.68
108.8	120.3	201.0	214.1	87.7	.89
109.7	119.9	202.8	215.4	88.4	.95
115.0	120.0	208.0	218.2	90.6	1.26

The Methylboron Fluorides

An attempt to employ boron fluoride in the study of the complex-bonding power of the oxygen atoms in methylboric anhydride, led only to a breakdown of this trimer, according to the

TABLE VIII

PREPARATION OF THE METHYLBORON FLUORIDES

Experiment		1	2	3	4	5
Reactants, cc.	$(CH_3BO)_3$	9.75	30	16.8	..	...
	BF_3	9.75	28.7	20.5	12.2	45.2
	$[(CH_3)_2B]_2O$	..	..	..	18.2	65.5
Temperature, °C.		25[a]	25	100	25	25
Time allowed, hr.		12	240	4	1	27
Reactants regained, cc.	$(CH_3BO)_3$	2.4	13	5.1	..	...
	BF_3	0	0	1.1[b]	0.6	0
Products, cc.	CH_3BF_2	13.6	42.2	27.5	..	...
	$(CH_3)_2BF$	..	..	..	21.6	110
Yields, %	Based on F	93	98	95	62	81
	Based on C	62	83	78	59	84

[a] The reaction was almost completed during two hours at −45°. [b] Here, the anhydride was regained by disproportionation of the non-volatile residue.

(idealized) equation $(CH_3BO)_3 + 2BF_3 \rightarrow 3CH_3BF_2 + B_2O_3$. The new compound, methylboron difluoride, thus was easily obtained in pure condition and in high yields. In spite of the break-down, the original purpose of the experiment was fulfilled, for the failure of the methylboron difluoride to form an addition compound with the residual methylboric anhydride demonstrated the weakness of the external bonding power of the oxygen atoms in that anhydride.

The series of gaseous compounds, BF_3, CH_3BF_2, $(CH_3)_2BF$, $(CH_3)_3B$, now was completed by the preparation of the other new member, dimethylboron fluoride, by a reaction which probably is to be written as $3(CH_3)_2BOB(CH_3)_2 + 2BF_3 \rightarrow 6(CH_3)_2BF + B_2O_3$. The dimethylboric anhydride used for this work was prepared by the action of phosphorus pentoxide upon dimethylboric acid,[10] as described by McKennon.[11] Here, again, the action of boron fluoride gave a high yield of an easily purified product.

The experimental details of the preparation of the methylboron fluorides are summarized in Table VIII.

The products were purified by the method of fractional condensation: methylboron difluoride passed a trap at −130°, and was efficiently condensed in a U-tube at −145° (through which boron fluoride passed easily); dimethylboron fluoride passed a U-tube at −120°, and was trapped at −135°. When there was no unused boron fluoride, either could be purified more simply, by distillation from a tube at −100°.

Molecular Weights.—A 12.1-cc. sample of methylboron difluoride weighed 34.6 mg.; the molecular weight thus was 64.1; CH_3BF_2 = 63.85. A 21.6-cc. sample of dimethylboron fluoride weighed 58.0 mg.; the molecular weight thus was 60.1; $(CH_3)_2BF$ = 59.87.

Analyses.—The methylboron fluorides were analyzed by treatment of measured samples with more than equivalent measured samples of zinc methyl. The resulting boron trimethyl was easily purified (by passage through a U-tube at −100°), and identified by its constant vapor tension of 31 mm. at −79°.[12] The unused zinc methyl was recovered (partly by heating the solid product *in vacuo* to 250°, whereby any CH_3ZnF was disproportionated); its purity was checked by its vapor tension of 123 mm. at 0°. The quantity of zinc methyl used up served to identify the compound, according to the equations $CH_3BF_2 + Zn(CH_3)_2 \rightarrow B(CH_3)_3 + ZnF_2$ and $2(CH_3)_2BF + Zn(CH_3)_2 \rightarrow 2B(CH_3)_3 + ZnF_2$. The data and results of the analyses are given in Table IX, which includes the experimental check of the method (by the use of boron fluoride).

The Vapor Tensions of the methylboron fluorides are given in Table X. The starred values in this table were used for calculating the equation $\log p = -(1204.0/T) + 1.75 \log T - 0.00684\ T + 5.9680$, from which the calculated values for CH_3BF_2 were obtained. The normal boiling point of methylboron difluoride thus is −62.3°; the molar heat of vaporization is 4750 cal., and the Trouton constant is 22.6 cal./deg. mole.

The data for dimethylboron fluoride determine the equation $\log p = 7.7370 - (1121.4/T)$, from which the normal boiling point is calculated to be −42.2°, the molar heat of vaporization, 5126 cal., and the Trouton constant, 22.2 cal./deg. mole.

The melting points of the methylboron fluorides were measured by the magnetic plunger method of Stock,[13] with the use of the carbon tetrafluoride vapor tension thermometer.[14] The values obtained for methylboron difluoride were −130.4° and −130.5°; those for dimethylboron fluoride, −147.4° and −147.3°.

Discussion

The chemical behavior of methylboric anhydride suggests a hexatomic ring structure like

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[10] Schlesinger and Walker, THIS JOURNAL, **57**, 624 (1935).

[11] F. L. McKennon, Ph.D. Dissertation, the University of Chicago Libraries, 1936.

[12] Stock and Zeidler, *Ber.*, **54B**, 534 (1921).

[13] Stock, *ibid.*, **50**, 156 (1917).

[14] Menzel and Mohry, *Z. anorg. allgem. Chem.*, **210**, 259 (1933).

TABLE IX

ANALYSES OF THE METHYLBORON FLUORIDES

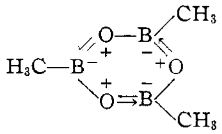
Substance analyzed	Sample, cc.	$Zn(CH_3)_2$, cc.	$B(CH_3)_3$, cc. Obsd.	$B(CH_3)_3$, cc. Calcd.	Recovered $Zn(CH_3)_2$, cc.	$Zn(CH_3)_2$ used, cc. Obsd.	$Zn(CH_3)_2$ used, cc. Calcd.
BF_3	6.3	16.4	5.9	6.3	7.1	9.3	9.5
CH_3BF_2	12.1	25.1	11.8	12.1	12.8	12.3	12.1
CH_3BF_2	6.8	13.4	6.9	6.8	6.3	7.1	6.8
$(CH_3)_2BF$	12.6	9.0	12.6	12.6	2.6	6.4	6.3
$(CH_3)_2BF$	10.6	8.2	10.3	10.6	2.6	5.6	5.3

TABLE X

VAPOR TENSIONS OF THE METHYLBORON FLUORIDES

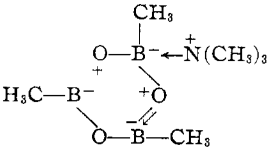
Methylboron Difluoride						Dimethylboron Fluoride		
t, °C.	p(mm.) (obsd.)	p(mm.) (calcd.)	t, °C.	p(mm.) (obsd.)	p(mm.) (calcd.)	t, °C.	p(mm.) (obsd.)	p(mm.) (calcd.)
−124	4.7	4.7	−91.1	116.4	115.5	−112	6.0	6.1
−121	6.4	6.7	−85.9	170.6	170.8	−96.0	25.2	25.4
−111.9	17.8	18.2	−80.9	242.7	242.9	−84.6	61.0	61.4
−98.6	62.4	62.8	−78.7	281.8*	281.8	−78.7	93.06	93.03
−95.7	80.0*	80.0	−69.0	524	519	−64.5	230.1	229.7
−94.2	90.0	90.8	−64.3	681*	681	−45.9	633	633

that already proposed for phenylboric anhydride[8] and for butylboric anhydride.[4] According to Bauer,[15] this structure recently has been confirmed by the electron diffraction method. The high thermal stability of this ring, and the lack of external bonding power on the oxygen atoms, suggest a resonating system of internal dative double bonds as the chief stabilizing influence in the molecule. The most probable structure thus would be written as

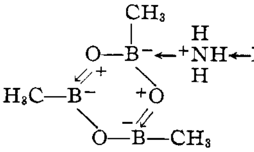
(I) 

It should be emphasized, however, that other structures, involving no double bonds, or cross-ring dative bonds, or even a double dative action by one oxygen atom, may well contribute to the resonance energy.

In terms of structural formula (I), the formation of the monotrimethylaminate may be interpreted as a displacement of one of the dative bonds. In the most probable case, the displaced bond would shift toward one of the other boron atoms, as indicated in structural formula (II); the accompanying shift of electron density toward the second and third boron atoms serves to explain the failure to add a second molecule of the amine. The same reasoning applies to the case of ammonia, with the difference that an explanation is needed for the secondary ammoniation. This is to be attributed to hydrogen bonding, as indicated in formula (III). Justification for this assumption is found in the fact that trimethylboron ammine forms the unstable secondary ammoniate $(CH_3)_3BNH_3{\cdot}NH_3$ (decomposition pressure, 24 mm. at −43°).[16] Such secondary ammoniation of ammoniates is fairly common, and in this case it must represent a case of hydrogen bonding unless one chooses to reject the Pauli exclusion principle, or to allow the displacement of a CH_3^- ion from the coördination sphere of boron. If the second ammonia molecule in $(CH_3BO)_3{\cdot}2NH_3$ were attached to a second boron atom in the ring, further ammoniation, by hydrogen bonding, would have been expected.



(II)



(III)

Now that the structural pattern of methylboric anhydride is known, it seems appropriate to assign to it the more descriptive name trimethyl triborine trioxane. This indicates its analogy to triborine triamine, for which the same pattern of dative double bonds has been suggested.[17]

Attempts to obtain the hydrogenated ring compound, triborine trioxane itself, by a B–H with B–CH_3 exchange, met with failure. Diborane could not be used, because the exchange reaction required too high a temperature. Tri-N-methyl triborine triamine[18] was effective at 140°, but

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[15] S. H. Bauer, private report on a sample of methylboric anhydride supplied by the author.

[16] Previously unpublished work of the author, in collaboration with Professor H. I. Schlesinger.

[17] Stock, Wiberg and Martini, *Ber.*, **63B**, 2932 (1930).

[18] Schlesinger, Ritter and Burg, THIS JOURNAL, **60**, 1296 (1938).

the product evidently was not sufficiently stable, at that temperature, to be saved.

The author wishes gratefully to acknowledge the courtesy of Professor H. I. Schlesinger, in whose private laboratory the major portion of this experimental work was done.

Summary

Methylboric acid, $CH_3B(OH)_2$, a volatile and unstable compound (not previously isolated) has been prepared and characterized. A thorough study of its dissociation, according to the equation $3CH_3B(OH)_2 \rightarrow (CH_3BO)_3 + 3HOH$, gave the result $\Delta F° = 9300 - 22.3\ T$, for the reaction in the vapor phase.

The anhydride of methylboric acid, $(CH_3BO)_3$ (b. p. 79°, m. p. −38°), is a ring trimer for whose thermal dissociation no evidence was found. It forms a mono-trimethylaminate, whose triple point is 67°, and (extrapolated) boiling point, 131° (highly dissociated vapor). No higher aminates are formed. A mono-ammoniate is formed, and a far less stable di-ammoniate; the latter evidently is formed by hydrogen bonding. It appears that only one boron atom (of the three in the ring) can coördinate with an external electron-donor atom.

The ring of methylboric anhydride is split by the action of boron trifluoride, to form the new compound methylboron difluoride (b. p. −62.3°, m. p. −130.5°), in excellent yields and without troublesome impurities. By the analogous cleavage of dimethylboric anhydride, another new compound, dimethylboron fluoride (b. p. −42.2°, m. p. −147.4°) is produced, also in good yields and in satisfactory condition. Both of these compounds appear to be permanently stable at room temperature.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 29, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Effect of Surface on Cool Flames in the Oxidation of Propane

BY R. A. DAY, JR., AND R. N. PEASE

The occurrence of successive "cool flames" during the oxidation of paraffin hydrocarbons is one of the many puzzling features of these reactions. The observations are of this sort. With a 1:1 propane–oxygen mixture, at about 400 mm. and 300°, in a 3.5-cm. Pyrex or silica tube, there will be first an induction period of perhaps five minutes duration; the pressure will then begin to rise slowly, and after several seconds a faint bluish luminescence will be seen near the center of the tube. This spreads toward the ends of the tube and then fades away in a few seconds. The phenomenon will be repeated several seconds later and at intervals until, in all, one may observe as many as eight or nine such periods of luminescence in the space of a minute or more. Coincident with each cool flame, a fairly sharp pressure rise occurs which is partially corrected in the succeeding period of quiescence.

It is to be emphasized that both the onset and the duration of the cool flames occupy measurable times. The phenomenon is sharply distinguished from the ignition which occurs at somewhat higher pressures with a bright yellow luminescence and the characteristics of a mild explosion.

It is evident that during the intervals between cool flames some intermediate is building up to a minimum concentration sufficient to produce the unstable state which leads to partial inflammation. Newitt and Thornes[1] suggest as a result of analyses conducted at different points in the process that the substances which are responsible are the "higher aldehydes," presumably acetaldehyde and propionaldehyde. These substances were shown to rise to a maximum concentration before the flame and to fall thereafter. On the other hand, Aivazov and Neumann[2] stress the importance of peroxides, and Neumann and Toutakin[3] go on to show that diethyl peroxide will in fact induce cool flames in butane–oxygen mixtures. However, similar experiments by Harris and Egerton,[4] in which propane was substituted for butane, revealed that even the ignition of diethyl peroxide failed to induce reaction in the propane–oxygen mixtures.

It is with this last result that we are especially

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(1) Newitt and Thornes, *J. Chem. Soc.*, 1656, 1665, 1669 (1937).

(2) Aivazov and Neumann, *Acta. Physicochim. U. R. S. S.*, **4**, 575 (1936).

(3) Neumann and Toutakin, *Compt. rend.*, **205**, 278 (1937).

(4) Harris and Egerton, *Proc. Roy. Soc.* (London), **A168**, 1 (1938).